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THE EVALUATION OF THE WATER QUALITY AND TRACE METAL CONCENTRATION THROUGH THE KIZILIRMAK RIVER OF TURKEY

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ABSTRACT

Kızılırmak is the longest river of Turkey (1355 km), and its catchment area is 78.000 km^2. The river starts at Kızıldağ in the Sivas province, it flows across the Central Anatolian plain and enters the Black Sea near the town of Samsun. Kızılırmak Delta occupies 50.000 ha and swamps, coastal lakes and lagoons. In this study, 10 different sampling points were selected according to pollution locality. The effects of anthropogenic activities, industrialization, urbanization on the bioaccumulation of heavy metals and nutrients in sediment and water through out from Sivas to Ankara of the rivers of Kızılırmak region were examined. Trace metal content (Al, Mn, Fe, Ni, Cd, Co, Cr, As, Pb, Hg, Cu) of water and sediment were determined by ICP-MS together with physico-chemical variables. According to Water Contamination Control Regulation 2004, Kızılırmak River has III-IV class water quality in terms of SO_4, Na and Al; II. Class in terms of Cl. Whereas the other metals were accumulated in the sediment of Kızılırmak river.

Keywords: heavy metal, water quality, criteria, Kızılırmak River, Turkey.

1 INTRODUCTION

Kızılırmak is the longest river of Turkey (1355 km), and its catchment area is 78.000 km^2. The river starts at Kızıldağ in the Sivas province, it flows across the Central Anatolian plain and enters the Black Sea near the town of Samsun. Kızılırmak Delta occupies 50.000 ha and swamps, coastal lakes and lagoons. The area includes very rich biological diversity (Akbulut & Akbulut 2009; Bakan et al. 2010).
Rapid industrialization and the discharge of potentially toxic trace metals into the river have caused many problems recently. Rivers are dynamic systems and may change in nature several times during their course because of changes in physical conditions such as slope bedrock geology (Bakan et al. 2010).

Metals in the river systems come naturally from sources as rock, erosion, weathering, soil erosion and dissolution of water soluble salts or artificial sources like domestic wastes or human activities. Most of the papers published on heavy metal bioaccumulation in the rivers (Hellawel 1988; Karadede and Ünlü 2000; Mahmood et al. 2000; Gümgüm at al. 1994, 2001; Akcay et al. 2003; Mendil et al. 2005; Karadede and Ünlü 2000, 2007; Barlas 1999, 2005; Alemdaroğlu et al. 2003; Dündar and Altundağ 2006). There are a few data on heavy metal concentrations in Kızılırmak River (Arman et al. 2007; Akbulut and Akbulut 2009; Akbulut and Tuncer 2010).

Trace metal content of water and sediment were evaluated together with water quality parameters during 2008-2009 in the Kızılırmak River. This information would be useful tool for the effective management, control with respect to the input and bioavailability of the metals together with the physico-chemical parameters.

2 MATERIALS AND METHODS

The water and sediment samples were collected from 10 different locations in Spring, Summer and December 2008-2009. Water samples were taken to 0.5 lt pre-cleaned polyethylene bottles and sediment samples were collected with an ekman sampler in cleaned 500 ml glass bottles. In addition one liter water samples were taken by using Ruttner sampler to measure main cations and anions such as NH_4, PO_4, NO_3, SO_4, Cl, HCO_3, Mg, Ca, K, Na. The heavy metals of water and sediment samples and chemicals have been measured in the Hacettepe University ICP-MS laboratory. The accuracy and analytical procedure was checked by analyzing the reference material DORM3 (National Research Council of Canada).

During the study EC, pH, temperature, salinity and dissolved O_2 have been measured on the selected stations using Consort C933 model sampler (in situ).

Totally ten sampling sites have been selected for the study. The names of the sites are Sarıoğlan (1), Vahşili (2), Near Sıvas City (3), Gülşehir (4), Göydan (5), Avanos (6), Durdullu (7), Bedirli (8), Sivas City Center (9), Himmetdede (10).

Sampling localities and study area was shown in the Figure 1. The measured physical and chemical variables have been given in the Figures 2-10 and Table 1; heavy metal results of water and sediment samples have been given in the Tables 2-3.

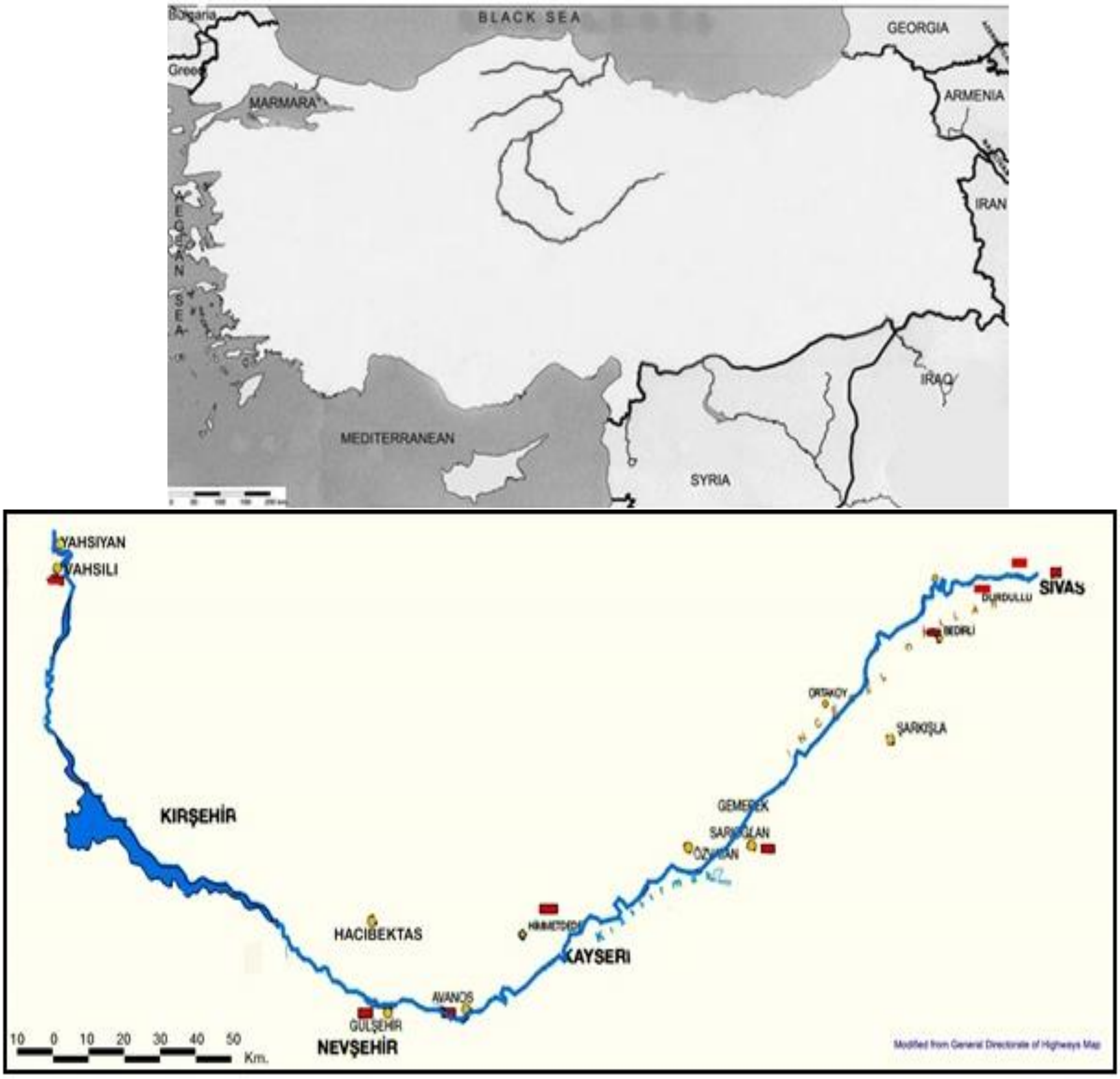


Figure 1. Study area and sampling locality

3 RESULTS AND DISCUSSION

According to the results, average pH was recorded as 7.18 in the S8 and 8.53 in the S5. pH was generally alkaline and recorded as between 7.5-8. Conductivity was between 1170 µS/cm in S5 and 3490 in the station 3. Electrical conductivity varied according to season which was high degree in summer and station too. Dissolved O_2 was varied 4.78 in the S5 and 13.8 in the S1 station. Figures 2-5 and Table 1.

According to the water chemical analysis PO_4 and NH_4 concentrations were < 0.001 mg/L at the ten sites. Distribution pattern of NH_4-N and PO_4 content were closely correlated. Salinity is a general term used to describe the presence of elevated levels of different soluble salts such as sodium chloride, magnesium and calcium sulfates and bicarbonates, in soil and water. The mean and maximum contents of the cations were Na> Ca>Mg>K as 103-173, 33.3-63, 2.32-7.57, 1.45-6.9 mg/L, respectively. The mean and maximum contents of the anions were SO_4> HCO3 > Cl > NO_3> NO_2 as 283-376, 156-245, 6.38-3.42, <0.01-6.667 mg/L, respectively. Figures 6-10 and Table 1.

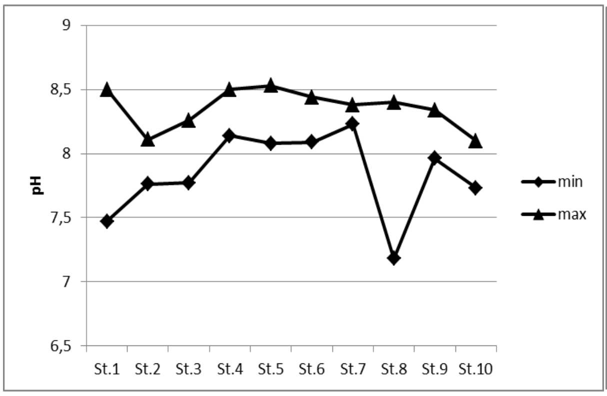
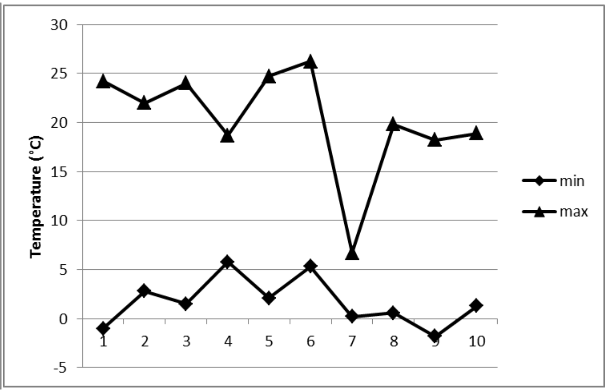


Fig.2



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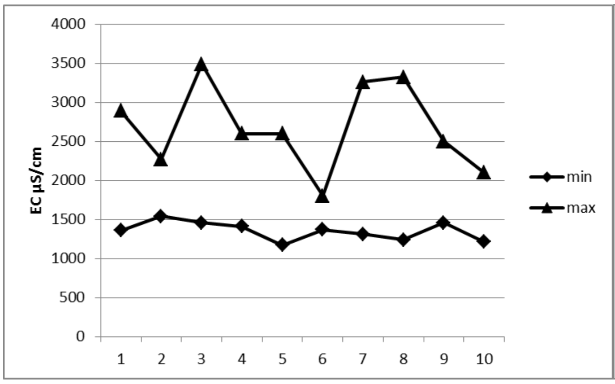

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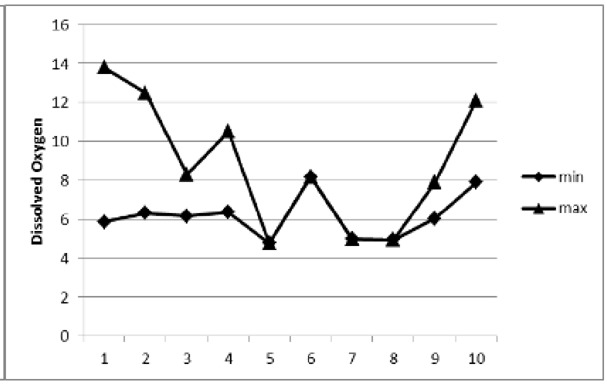


Fig. 5.

Figure 2-5. Measured min-max. pH, Temperature, Conductivity and Dissolved Oxygen at the stations.

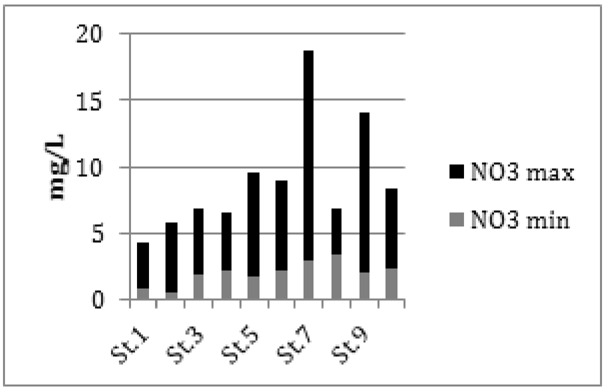
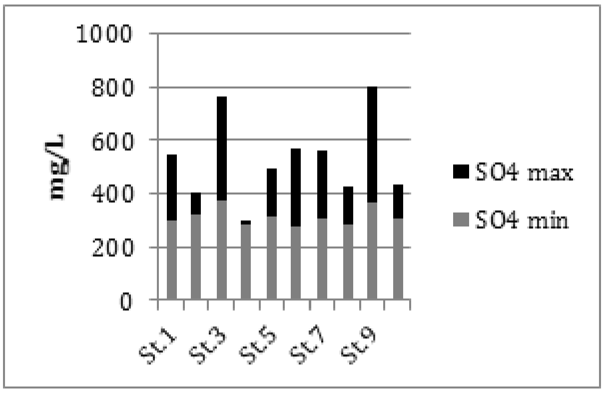


Fig.6.



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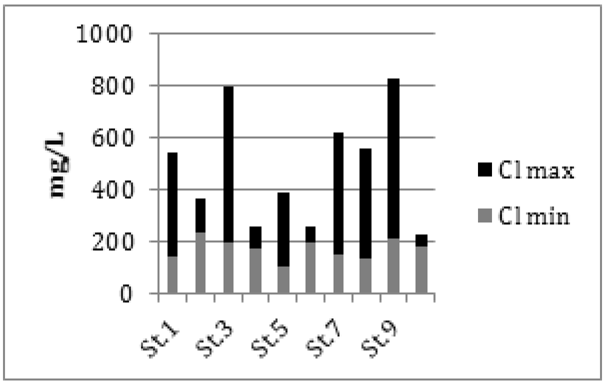

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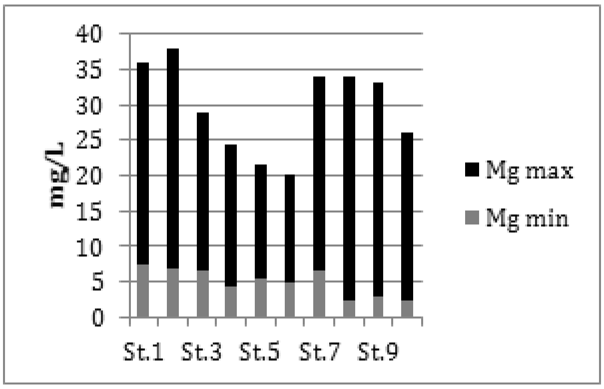

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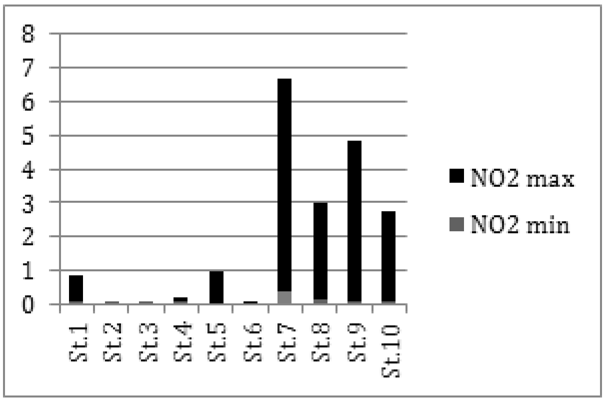

Fig.10.

Figure 6-10. Measured mean chemicals (NO_3, SO_4, Cl, Mg, NO_2) at the stations (mg/L)

The sulphate general use water quality standard of 500 mg/L with an aquation depends on chloride and hardness concentration. For example, high chloride and TDS concentration was highly toxic to aquatic life; however high sulphate with TDS concentration is non toxic (Iowa's water quality standard review,2008).

These metals were arranged according to metal concentration from the highest to lowest values as Al>Fe>Zn>Pb>As>Mn>Ni>Se>Cr>Co>Hg in the surface water samples.

Determined heavy metals results have been slightly changed in surface water at the stations and seasons too. Mean Al concentration was 0.241 mg/L in May; 139-160.6, 108-158.3 mg/L in August and December, respectively. The lowest concentration was observed in the 3S station while the highest levels were in 5S and 8S stations. Fe was 0.009 mg/L at 9S which is the lowest value, and was 1.95 mg/L at 2S as the highest value in May samples, while 0-264.2 mg/L in August and under detection level at the 4S and 615.9 at 6S in December sampling. Zn was min 0.068 at 10S and max. 0.127 at 9S in may while under the detection level in August and December. As was under the detection level in May, whereas 5.56 mg/L in the 5th Station; 14.47 mg/L in 2nd Station as the highest level in August and 7.47 mg/L in 1st Station while 20.18 mg/L in the 7. Station. Mn min 0.005 mg/L at 1S and max 0.431 mg/L at 7S while nd-5.645 mg/L and 0.6-10.73 mg/L in August and December samples respectively. Ni was under detection level in December while 0.012-0.037 mg/L in May and nd-8.023 mg/L 7S in August. Cd concentration was 0.025 mg/L in May; 0. 261-1.385 mg/L in August and 0.243 -1.346 mg/L in December. Mean Cd was 0.57 mg/L in these two sampling months while 0.025 mg/L in May. Cd didn't change between the stations either. Whether Co was below the detection level at all the stations in May samples, 0.825 as min at 2S and 2.602 as max level at 9S in the August samples and 0.614 at 2S and 0.614 at 6S in December. Co was observed the highest in August samples. Pb was measured as min. 0.0015 at 10S and max. 0.079 at 5S in May; between 3.7-4.1 in August and 7.79-8.77 in December as the highest. Pb was higher in December, August and May respectively.

Determined mean heavy metal concentrations in the surface water samples have been given in the Table 2. Metal concentrations of the sediment samples can be arranged from the highest to lowest values as Al > Fe >Mn >Cr >Ni >Zn >As >Cu > Co >Pb >Cd >Hg . Cd, Hg and Pb concentrations were higher at all the stations in May samples, the other metals were higher in August and December samples. But there is no significant differences between the stations and sampling time. Determined mean heavy metal concentrations in the sediment samples have been given in the Table 3.

Trace element concentrations of river basins depend not only on industrial and household waste inputs but also on the geochemical composition of the area. High concentration of Zn, Mn, Cr are thought to be resulted from anthropogenic sources. Water pollution is any contamination of water with chemicals or other foreign substances that are detrimental to human, plant, or animal health. These pollutants include fertilizers and pesticides from agricultural runoff; sewage and food processing waste; lead, mercury, and other heavy metals; chemical wastes from industrial discharges; and chemical contamination from hazardous waste sites.

In Turkey many studies have been done on the heavy metal pollution in the different river systems. (Akcay, Oguz, and Karapire, 2003) show that the pollution levels are significant especially for Pb, Cr, Mn and Zn in the Gediz river and Co, Mn, and Zn in the Big Meander river.

Dundar and Altundağ (2007) studied the Sakarya River. The results show that there were significant differences based upon sampling times, regions, sediment and water samples. The mean levels of copper, nickel, chromium, lead, cadmium, zinc for sediment samples are; 4.630 $\mu g\ g^{-1}$, 13.520 $\mu g\ g^{-1}$, 8.780 $\mu g\ g^{-1}$, 2.550 $\mu g\ g^{-1}$, 9.990 $\mu g\ g^{-1}$ and for water samples are; 0.851 $\mu g\ g^{-1}$, 1.050 $\mu g\ g^{-1}$, 0.027 $\mu g\ g^{-1}$, 1.786 $\mu g\ g^{-1}$, 0.236 $\mu g\ g^{-1}$, 0.173 $\mu g\ g^{-1}$, respectively.

Barlas (1999) was studied the heavy metal concentration of water, sediment and fish species of Sakarya River. The results show that mean concentrations of lead, cadmium and cobalt increased in sediment samples in October and August. In water samples cadmium and cobalt increased in October, whereas lead and copper increased in August. In Tigris River Cd, Cu, Mn, Ni, Zn and Fe values were found to be high in spring and summer (Karadede Akın and Ünlü 2007).

Bakan et al. (2010) were studied the spatial and seasonal trends in water discharge, nutrients, trace metals and quality index of nine sites along Kızılırmak River on Black Sea coast and reservoir. The result show that the river has medium quality of lead pollution and indicates eutrophic conditions where algal growth and blooms can occur.

Okuş et al. (2007) were observed Pb, Cd and Hg concentrations of Southern Marmara rivers and high metal concentration were observed in the Erdek bay waters.

4 CONCLUSION

Ministry of Agriculture and Rural Affairs, Water Control Administrative Regulations (2004) was classified the natural waters from I to IV level according to water chemicals and heavy metal concentrations. According to Water Contamination Control Regulation 2004 Kızılırmak River has III-IV class water quality in terms of SO_4, Na and II. Class in terms of Cl. The heavy metal results showed that Kızılırmak Stream water is in the class of I with respect to Cd, Cr, Mn, Fe, Co, Hg, Zn, Pb, As, Ni and in the class of IV for Al. (TKB 2004; EPA 2006).

The results show that mean concentrations of lead, cadmium and Mercury increased in sediment samples in May whereas the others were accumulated in August and October. But statistically the levels of the metals among stations were insignificant ($P<0.05$).

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Table 1. Minimum and maximum chemical and physical variables of ten different location of surface water (mg/L)

Min-Max.	pH	EC µS/cm	Temperature°C	Diss.O2	Cl	NO2	NO3	SO4	HCO3	Na	K	Mg	Ca	PO4	NH4
1.Sta.	7,47-8,50	1360-2890	(-1)- 24,20	5,88-13,8	141,2-546,5	0,09-8-0,860	0,860-4,38	296,9-546,5	214-270	109-378	3,58-188	7,57-36	39-274	<0,01	<0,01
2.Sta.	7,76-8,11	1540-2270	2,8-22	6,33-12,50	234,4-363,9	<0,01	0,638-5,79	323-406,8	156-196	173-268,5	6,9-268	6,73-37,8	63-126	<0,01	<0,01
3.Sta.	7,77-8,26	1460-3490	(-1,5)-24	6,17-8,30	199-799,6	<0,01	1,86-6,88	376,4-764,6	212-224	143-553	6,9-453	6,54-29	36-380	<0,01	<0,01
4.Sta.	8,14-8,50	1410-2600	5,8-18,7	6,36-10-50	174,3-260,6	0,088-0,230	2,24-6,64	286-296	218-227	130-195	2,74-195	4,45-24,5	38-163	<0,01	<0,01
5.Sta.	8,08-8,53	1170-2600	2,1-24,7	4,78	101,4-389,9	<0,01-1,00	1,72-9,60	310,8-490,9	188-297	148-288	3,98-195	5,56-21,5	37-246	<0,01	<0,01
6.Sta.	8,09-8,44	1370-1800	5,3-26,2	8,18	197,9-258,9	<0,01-0,016	2,27-8,96	275,6-570	225-245	149-218	1,45-288	4,81-20	37-165	<0,01	<0,01
7.Sta.	8,23-8,38	1310-3260	0,2-6,7	5	153,6-622,4	0,393-6,667	3,02-18,79	305-564	245-251	143-410	3,42-178	6,56-34	37,1-304	<0,01	<0,01
8.Sta.	7,18-8,40	1240-3320	0,6-19,8	4,95	139,3-555,9	0,132-3,01	3,42-6,92	283-424	205-269	115-542	1,76-410	2,43-34	36-383	<0,01	<0,01
9.Sta.	7,96-8,34	1460-2500	(-1,8)-18,2	6,04-7,90	210-828,6	0,096-4,856	2,06-14,08	367-805	206-245	137-328	1,82-454	2,94-33	36-182	<0,01	<0,01
10.Sta.	7,73-8,1	1215-2100	1,3-18,9	7,90-12,11	180-255	0,063-2,780	2,33-8,35	308-431	177-214	103-450	2,91-186	2,32-26	33,3-391	<0,01	<0,01

Table 2. Mean metal levels with standart errors in the ten different location of surface water (µg/L)

	Al	SD	Cd	SD	Cr	SD	Mn	SD	Fe	SD	Co	SD	Hg	SD	Se	SD	Zn	SD	Pb	SD	As	SD	Ni	SD
1.Sta.	127,23	±23,7	0,73	±0,41	1,85	±1,44	4,55	±4,34	199,3	±81,3	1,24	±0,54	0,02	±0,03	1,84	±1,65	40,67	±70,44	5,79	±1,87	9,46	±2,80	2,47	±2,50
2.Sta.	187,03	±110,6	0,29	±0,06	0,48	±0,03	12,71	±15,91	87,3	±51,2	0,72	±0,15	0,02	±0,03	3,04	±2,37	59,33	±102,77	7,50	±3,09	13,86	±0,87	0,57	±0,98
3.Sta.	172,30	±72,5	0,52	±0,32	3,35	±3,08	4,22	±2,26	167,5	±136,6	1,81	±0,91	0,02	±0,03	1,99	±2,09	42,00	±72,75	5,65	±2,35	10,83	±7,02	3,22	±3,63
4.Sta.	203,13	±134,8	0,25	±0,01	0,00	±0,63	3,97	±6,36	13,8	±19,6	1,03	±0,26	0,03	±0,02	3,06	±3,92	45,33	±78,52	4,67	±2,89	8,78	±0,16	0,60	±1,04
5.Sta.	135,33	±18,6	0,88	±0,66	1,45	±1,58	5,29	±6,02	52,8	±22,7	1,44	±0,28	0,03	±0,01	2,18	±1,92	39,00	±67,55	6,69	±2,64	8,48	±4,12	1,38	±2,02
6.Sta.	132,13	±19,7	0,63	±0,06	0,64	±1,43	1,87	±1,66	346,6	±380,8	1,24	±0,31	0,02	±0,02	1,58	±1,93	46,00	±79,67	5,65	±2,00	8,69	±1,17	0,66	±0,70
7.Sta.	247,23	±196,3	0,79	±0,84	4,68	±5,33	3,69	±1,63	232,7	±294,5	1,61	±0,51	0,02	±0,03	1,77	±0,97	43,00	±74,48	6,09	±2,78	17,83	±3,33	3,54	±4,09
8.Sta.	217,67	±163,8	0,67	±0,34	0,26	±0,27	20,13	±32,82	12,2	±17,2	1,58	±0,38	0,04	±0,01	2,22	±2,86	43,67	±75,63	6,99	±2,69	13,60	±0,72	1,79	±1,73
9.Sta.	126,37	±17,7	0,52	±0,24	1,22	±0,34	8,87	±7,24	99,7	±40,5	1,93	±0,95	0,03	±0,04	2,00	±2,58	42,33	±73,32	4,72	±3,30	10,81	±5,70	2,75	±3,39
10.Sta.	130,83	±37,5	0,47	±0,06	1,14	±0,47	7,38	±8,33	92,2	±19,7	1,00	±0,14	0,04	±0,02	3,00	±2,63	22,67	±39,26	4,75	±3,70	12,82	±7,59	0,40	±0,69

Table 3. Mean metal levels with standart errors in the ten different location of sediment (µg/g)

	Al	SD	Cr	SD	Mn	SD	Fe	SD	Co	SD	Zn	SD
1.Sta.	21523,3	±6353,7	96	±68,08	555,3	±190,7	22403,3	±9378,2	11,23	±8,28	57,17	±19,94
2.Sta.	25400	±25891,8	211,8	±46,21	639,6	±266,9	26835	±17887,9	22,2	±6,77	75,07	±52,55
3.Sta.	31876,6	±4151,3	128,2	±9,48	695,4	±252,8	27961,6	±4849,8	17,73	±1,38	96,2	±13,6
4.Sta.	24650	±6526,2	118	±61,62	469,3	±185,5	19486,6	±7118,2	12,9	±9,35	114,9	±82,3
5.Sta.	22208,3	±9658,5	100,1	±62,26	511,3	±198,1	25340	±12517,6	13,93	±9,87	64,02	±40,72
6.Sta.	20006,6	±4687,9	103,2	±26,16	489,4	±69,3	21596,6	±7233,8	12,23	±4,43	86,03	±12,24
7.Sta.	41950	±19786,4	156,9	±64,74	672,3	±114,8	33466,6	±4254,7	24,92	±6,66	75,6	±47,47
8.Sta.	21168,3	±6000,9	53,6	±3,61	509,1	±189	19116,6	±9893,9	6,99	±2,05	69,07	±10,22
9.Sta.	21318,3	±520,8	89	±12,45	484,4	±131	24920	±5499,3	11,09	±2,76	54,82	±35,47
10.Sta.	15980	±9426,2	63	±53,47	356	±130	14353,3	7318,3	7,61	±6,71	76,15	±44,34

	Hg	SD	Se	SD	As	SD	Cu	SD	Ni	SD	Pb	SD
1.Sta.	10,41	±14	2,96	±2,04	47,08	±1,68	6,85	±5,56	80,9	±87,64	11,68	±15
2.Sta.	13,63	±19,5	3,36	±0,02	51,66	±5,65	20,32	±7,58	245	±55,79	14,77	±19,7
3.Sta.	11,69	±16,7	3,17	±2,35	44,62	±1,59	6,51	±1,94	172,5	±7,6	12,63	±17,6
4.Sta.	12,07	±17,4	4,38	±1,75	39,3	±6,42	85,48	±120,5	124,9	±112,32	35,88	±50,5
5.Sta.	19,92	±30,6	4,18	±0,88	36,27	±0,71	11,16	±2,35	121,8	±118,36	14,72	±20,3
6.Sta.	13,19	±19,4	2,5	±1,53	38,46	±1,48	10	±5	87,8	±26,55	13,99	±19,3
7.Sta.	61,57	±58,1	2,95	0,64	52,41	±18,59	7,63	±7,46	205,8	±162,88	16,48	±22,3

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